

N-Scaling Materials Response by Density Matrix Perturbation Theory

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During the last decade a new computational approach has evolved in electronic structure theory, where no critical part of a calculation is allowed to increase in complexity more than linearly, $O(N)$, with system size, N [1]. This linear scaling electronic structure theory extends conventional tight-binding, Hartree-Fock, or Kohn-Sham methods to the study of very large complex systems previously out of reach. This is critical for applications to new important areas of research, such as biology, medicine, and nanoscience, which requires the ability to handle much larger systems than previously possible.

Until recently most attention was focused on linear scaling $O(N)$ methods for calculating the ground state electronic energy. However, an important problem that so far has received little attention is the $O(N)$ computation

of materials response properties, such as interatomic potentials, vibrational frequencies, the polarizability, nuclear magnetic resonance, and Raman intensities.

We have introduced a new and surprisingly simple reduced complexity quantum perturbation theory [2, 3]. The approach is based on $O(N)$ spectral purification projection schemes for the zero-temperature density matrix [4, 5]. The new perturbation theory makes it possible to calculate the adiabatic response properties for nonmetallic materials to any order within linear scaling effort.

The numerical efficiency of density matrix purification projection methods is based on the quantum locality (or nearsightedness) of nonmetallic systems, manifested in the approximate exponential decay of the density matrix with interatomic separation. Using efficient sparse matrix algebra, neglecting matrix elements below a chosen numerical threshold, the density matrix can be constructed with a computational cost that scales linearly with system size.

The general idea behind purification is that the density matrix D can be described recursively as

$$D = \theta(\mu I - H) = \lim_{n \rightarrow \infty} F_n(F_{n-1}(\dots F_0(H)\dots)), \quad (1)$$

where $F_n(F_{n-1}(\dots F_0(H)\dots))$ is an iterative expansion of the Heaviside step function $\theta(\mu I - H)$. The functions F_n are low order

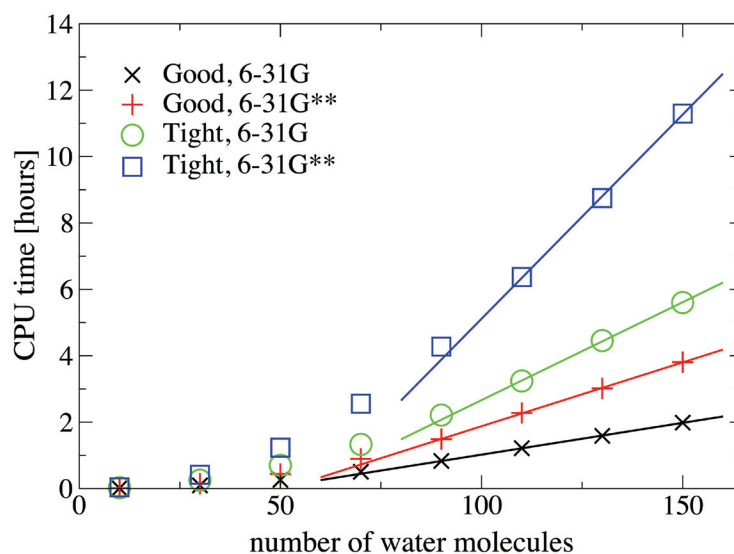


Figure 1—
The computational cost for the first hyperpolarizability of water clusters as a function of basis set and cluster size [6].

polynomials, projecting eigenvalues to fix points at 0 for unoccupied states and to 1 for occupied states, thereby “purifying” the approximate density matrix. By choosing the purification projectors F_n to be polynomials, only matrix-matrix operations have to be performed. This is achieved with linear scaling $O(N)$ complexity for sufficiently sparse systems.

The main problem with density matrix perturbation theory is the discontinuous relation between the zero temperature density matrix and the Hamiltonian given by the step function in Eq. 1. This makes an expansion of D around a perturbation in H difficult. At finite temperatures the discontinuity disappears, but instead the analytic Fermi-Dirac distribution involves problems with matrix exponentials and the chemical potentials. However, within the recursive purification scheme an initial perturbation in H can be carried through at each projection level, either exactly or to any order. The resulting perturbed projection scheme provides an efficient technique for the calculation of materials response properties within a reduced complexity formalism [2, 3].

Our new perturbation theory has been implemented in MONDOSCF, a suite of parallel linear scaling program for the ab initio calculation of electronic structure properties. Linear scaling complexity was demonstrated for the computation of higher order response properties of 3D structures. Figure 1 shows the computational cost for calculating the first electric hyperpolarizability of large water clusters by solving the coupled perturbed self-consistent field equations [3, 6]. After about 50–100 water molecules the computational cost scales approximately linearly with system size.

The locality of the density matrix is described by the approximate exponential decay of its matrix elements as a function of interatomic separation. This behavior is found also for the density matrix derivatives corresponding to the polarizability and hyperpolarizabilities, as illustrated in Fig. 2.

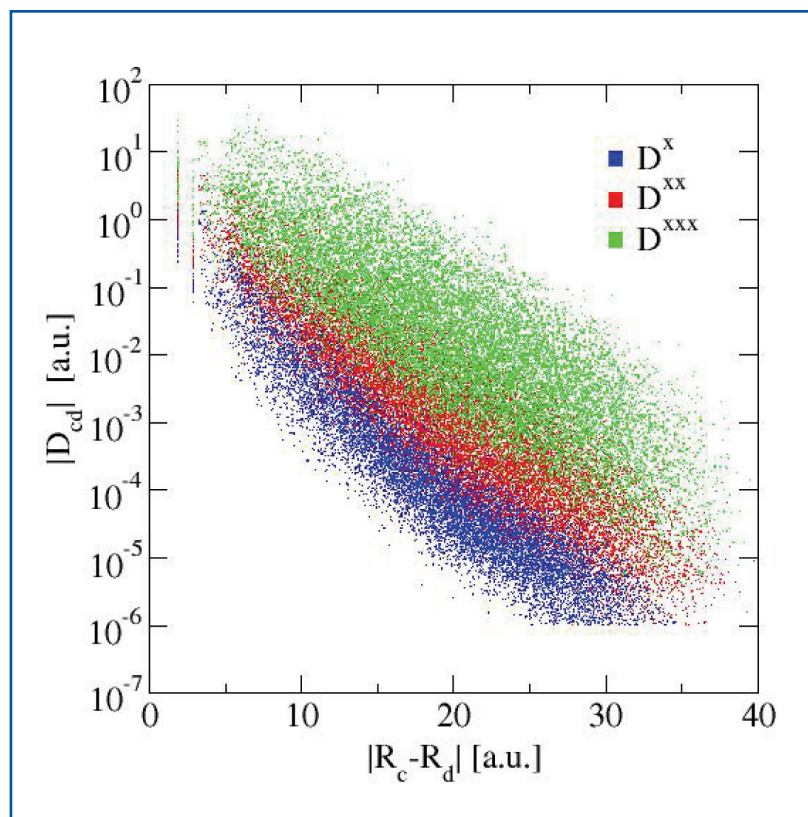


Figure 2—
The approximate exponential decay of the density matrix and its derivatives as a function of interatomic separation.

The density matrix perturbation theory can be applied in many contexts and we are currently extending the theory to new problems, including structural response within nonorthogonal representations for the calculation of vibrational frequencies.

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